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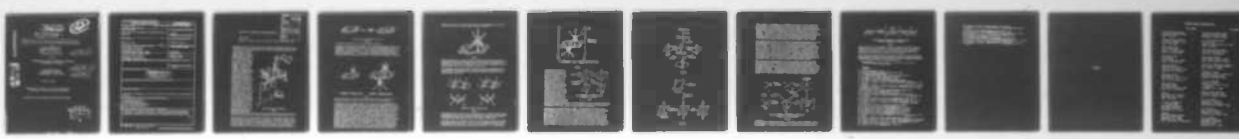

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10 Minoru Tsutsui

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A broad review on current progress in chemistry of organometalloporphyrins is reviewed. An emphasis was placed on the development of metallocarbonyl-porphyrins, dinuclear metalloporphyrins and "Skewered metalloporphyrins".

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NEW TRENDS IN THE CHEMISTRY OF ORGANOMETALLOPORPHYRINS

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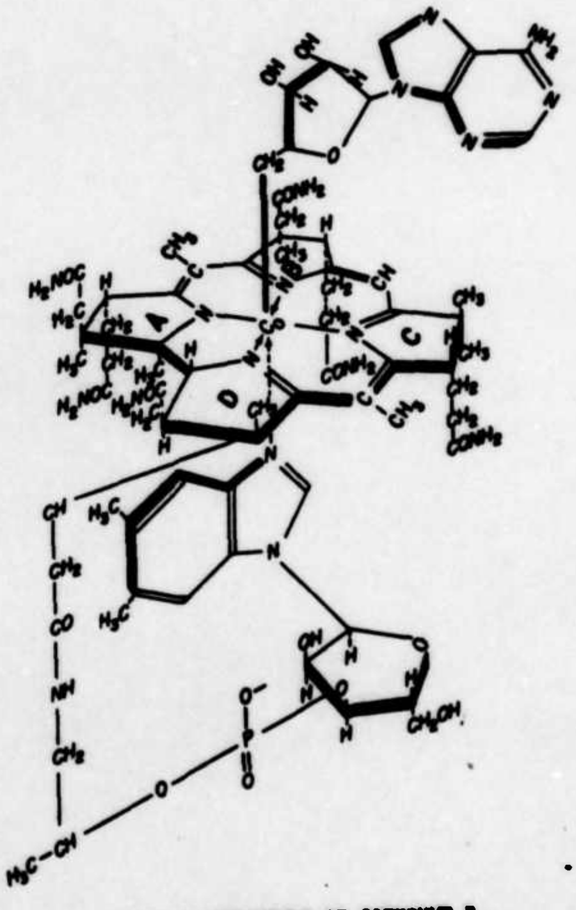
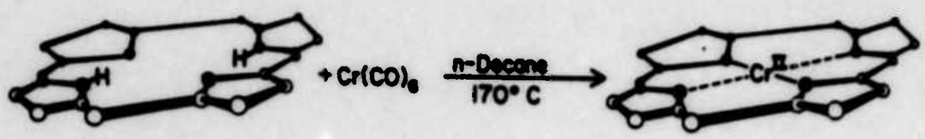
Organometalloporphyrins in general are defined as synthetic metalloporphyrin complexes containing at least one direct metal-carbon bond. However, the coenzyme fo vitamin B_{12} (Figure 1) containing an adenosyl group linked to cobalt by a direct cobalt-carbon σ-bond is the first example of a naturally occurring organometallocorrin complex (similar to organometalloporphyrins in molecular structure) and the first-known stable organocobalt derivative.[2,3] The determination of the structure of the vitamin B_{12} coenzyme by x-ray crystallography[4,5] prompted several studies of the synthesis and properties of cobalt-alkyl compounds. Johnson and his co-workers[6-9] extended their studies to the porphyrin series by reaction of pyridinobromocobalt(III)aetioporphyrin-I with a variety of alkyl- and aryl-magnesium halides in anhydrous 1,2-dimethoxyethane (DME) to give the corresponding alkyl- and aryl-cobalt(III) derivatives.[8,9] Ethyl and p-tolyl-iron(III) derivatives[7] of aetioporphyrin-I were also prepared by a similar method. The first-row transition metal derivatives of organometalloporphyrins were thus synthesized for the first time. In an alternative synthesis, Johnson and his co-workers were also able to prepare the identical alkyl cobalt(III)aetioporphyrin-I complexes as that mentioned above, by reduction of cobalt (II)aetioporphyrin-I with 1% sodium amalgam in DME to form cobalt(I) species,[7] which then react with alkyl halides to give the final products. This method was also used for the preparation of hydroxyalkyl-cobalt(III)aetioporphyrin-I complexes.[8] Both the cobalt(III) and the iron(III) organometalloporphyrins are sensitive to light, especially in solution, and decompose by homolytic fission of the metal-carbon bond.



SPATIAL STRUCTURE OF COENZYME B_{12}

FIGURE 1

The use of metal carbonyls for the insertion of metal ions into porphyrins was first introduced by Tsustui and his co-workers[10,11] in 1966(Figure 2). This method is probably one of the most important developments in porphyrin chemistry within the last two decades. In addition to a number of previously reported metalloporphyrins, the reaction of metal carbonyls and metla carbonyl halides[12,21,24-29] with neutral porphyrins has lead to the synthesis of new metalloporphyrin complexes of chromium, molybdenum, technetium, ruthenium, rhodium, rhenium and iridium.[10-32] Except for the chromium and molybdenum complexes, carbonyl groups

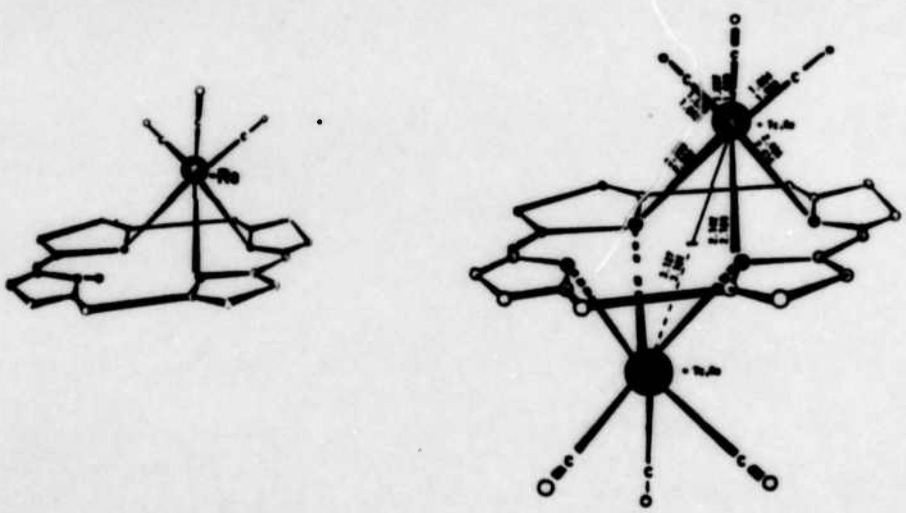


USE OF $Cr(CO)_6$ FOR INSERTION OF Cr^{II} TO PP

FIGURE 2

are retained by the metals in the new metalloporphyrin complexes.

By reaction of dirhenium decarbonyl, $Re_2(CO)_{10}$, or ditechnetium decacarbonyl, $Tc(CO)_{10}$, with mesoporphyrin IX dimethylester, H_2MPIXDME, in refluxing decalin under argon, Tsutsui and his co-workers have successfully prepared two unusual rhenium organometalloporphyrins[31,32] (H-MP)$Re(CO)_3$, I, and MP$[Re(CO)_3]_2$, II, a pair of technetium organometalloporphyrins,[33,34] (H-MP)$Tc(CO)_3$, III, and MP$[Tc(CO)_3]_2$, IV, and a mixed rhenium technetium organometalloporphyrin[13], $(OC)_3$ReMPTc$(CO)_3$, V. A single crystal x-ray diffraction analysis of μ-[*meso*-tetraphenylporphinato]bis[tricarbonylrhenium(I)],[30] TPP$[Re(CO)_3]_2$, VI, (Figure 3), has shown



Porphyrin – Tridentate Ligand Porphyrin – Hexadentate Ligand

FIGURE 3

that each rhenium ion is bonded to three nitrogen atoms and that two rhenium atoms are bonded to one porphyrin on opposite sides of the plane of the porphyrin molecule.

The metal ions in these complexes, I-VI, sit out of the plane of the porphyrin molecule. The monorhenium and monotechnetium complexes, I and III, where the porphyrin moiety acts as a tridentate ligand, resemble Fleischer's proposed "sitting-atop complex"[38,39] and are good models for the intermediates in the insertion of a metal ion into porphyrin.[40] The dirhenium, ditechnetium, and mixed rhenium-technetium organometalloporphyrin complexes, II, IV, V, and VI, where the porphyrin moiety acts as a hexadentate ligand, are examples of the first isolated stable homo- and hetero-dinuclear organometalloporphyrin complexes.[13,32] The monorhenium porphyrin complex, I, reacts with $Re_2(CO)_{10}$ or $Tc_2(CO)_{10}$ in refluxing decalin to form the dirhenium porphyrin complex,[31] II, and the mixed rhenium technetium porphyrin complex,[13] V, respectively. Replacement of the pyrrolic proton (N-H) of the monorhenium porphyrin complex by other metal ions such as Ag^+, Hg^{2+}, and Pb^{2+}, has resulted in unstable complexes.[32] The monotechnetium porphyrin complex, III, (Figure 4), behaves in a different manner by disproportionating to form a ditechnetium porphyrin complex, IV, and the free porphyrin, H_2MPIXDME, by heating in refluxing decalin[34]. This unusual coordination phenomenon has never been reported. Such a reaction was not observed on heating monorhenium porphyrin complex, I, in refluxing decalin.[31,32] It seems that both the rhenium and technetium dimetalloporphyrin complexs are are thermodynamically more stable than the monometalloporphyrin complexes, because a reverse reaction of MP$[M(CO)_3]_2$ to (H-MP)-$M(CO)_3$,

(M=Re or Tc), could not be detected between $MP[M(CO)_3]_2$ and $H_2MPIXDME$ in refluxing decalin for either the rhenium of technetium dimetalloporphyrin complexes.[31-34]

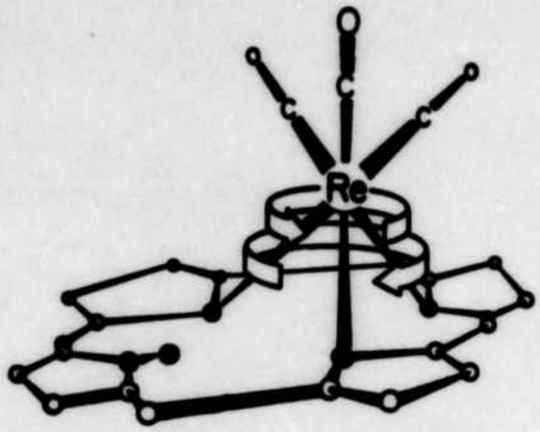
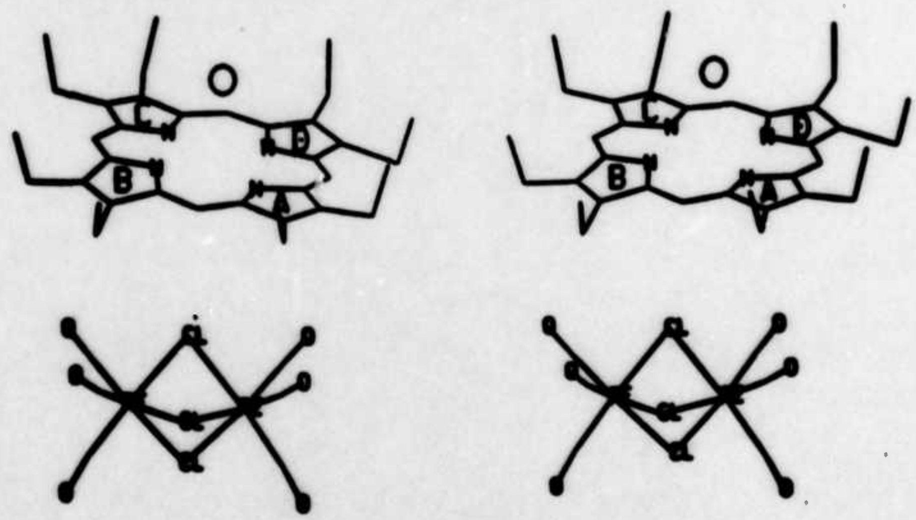


FIGURE 4

Temperature-dependent ^1H nmr spectral changes for $HTPPRe(CO)_3$ and $HMPRe(CO)_3$ dissolved in 1,1,2,2-tetrachlorethane showed fluxional behavior of $Re(CO)_3$ group. This phenomenon is best explained by the intramolecular rearrangement of the metal carbonyl group among the four ring nitrogens of porphin and also movement of the N-H; it can also be regarded as as intramolecular substitution at rhenium or technetium, (Figure 4).[35]

We have prepared a new salt type complex of porphyrins, monocation octaethylporphyrin tri-μ-halogeno-hexacarbonyldirhenate(I) from the reaction of $Re(CO)_5Cl$ and H_2OEP in a 2:1 mole ratio in decalin. The structure of the complex was elucidated by the x-ray diffraction analysis method, (Figure 5).[36]

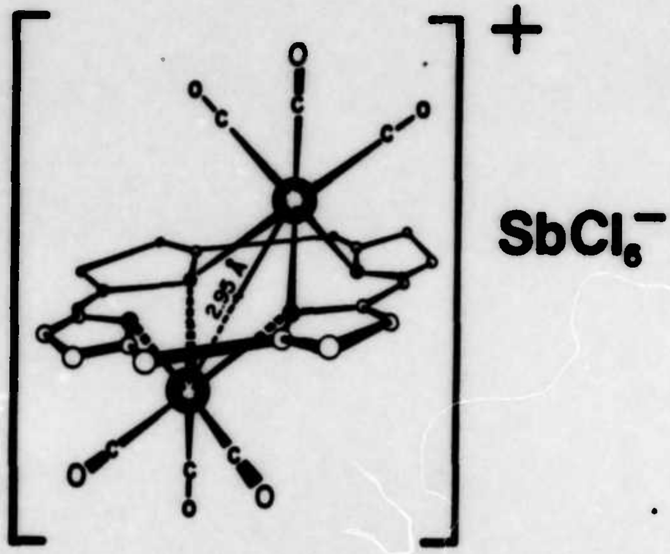


STRUCTURE OF $(H_3OEP)^+[Re_2(CO_6)Cl_3]^- H_2O$

FIGURE 5

$[Re(CO)_3]_2TPP$ has been oxidized by $SbCl_5$ in dichloromethane to yield $[Re(CO)_3Cl]_2TPP \cdot 2SbCl_6$ and $[Re(CO)_3][Re(CO)_3Cl] \cdot SbCl_6$. An x-ray determination of the structure of these complexes provides definite evidence for a "skewered complex", that is a metalloporphyrin in which a metal-metal bond exists through the "hole" of the macrocycle, (Figure 6).[37]

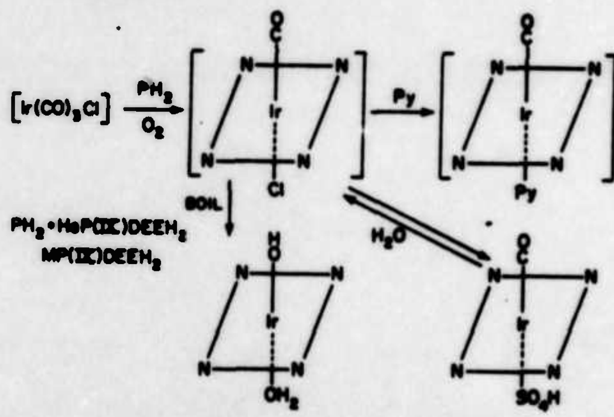
Two different methods were employed by Fleischer and his co-workers in preparing the rhodium and iridium porphyrin complexes.[24,25] In one, the freshly prepared metal carbonyl halides, $[Rh(CO)_2Cl]_2$ and $[Ir(CO)_3Cl]$, were allowed to react with the porphyrins in glacial acetic acid solution to form the respective metalloporphyrins, (Figure 7). In the second method,



First Skewered Complex (Radical Metalloporphyrin)

FIGURE 6

the cyclooctene complexes of rhodium and iridium were found to be reactive intermediates useful in the metalloporphyrin formation, (Figure 8). In both methods, incorporation of rhodium into the porphyrin was more readily achieved than was that of iridium. It is of interest that in the metalloporphyrins prepared by these methods, the iridium porphyrins retain the carbon monoxide ligand while rhodium and other metals do not.[14,21] The carbon monoxide is very tightly bound to the iridium porphyrin moiety; heating, pumping, boiling in pyridine, or reprecipitating from concentrated sulfuric acid solution does not remove the carbonyl group from the complex.[24]



REACTION SCHEME FOR IRIDIUM PORPHYRIN PREPARED VIA $Ir(CO)_3Cl$

FIGURE 7

By the reaction of $[Rh(CO)_2Cl]_2$ with *meso*-tetraphenylporphine, H_2TPP, in refluxing benzene, two stable organometalloporphyrin derivatives of rhodium, $Rh^{III}CO(TPP) \cdot Cl$ and (σ-phenyl)Rh^{IV}-(TPP) $\cdot$ Cl, were separated by chromatography on an alumina column by Fleisher and his co-workers[21,26].

Yoshida and his co-workers were able to prepare two novel dinuclear rhodium(I) organometalloporphyrin complexes,[28,29] VII and VIII, by modifying Fleischer's reaction conditions for the preparation of $Rh^{III}CO(TPP) \cdot Cl$ and (σ-phenyl)Rh^{IV}(TPP) $\cdot$ Cl in refluxing benzene.[21,26] Octaethylporphyrin, $OEPH_2$, or (N-methyl) octaethylporphyrin reacts with $[Rh(CO)_2Cl]_2$ in benzene solution at room temperature under nitrogen atmosphere to produce VII and VIII. From the spectral data and the experimentaly determined molecular weight[29] VII was formulated as an acid, $H^+[OEP \cdot Rh_2(CO)_4Cl]^-$, which contains a Rh-Cl-Rh bridge. The proton nmr and infrared spectral data indicate that the $[Rh(CO)_2Cl]_2$ moiety is maintained and the N-H and $N-CH_3$ bonds exist in VII. Since the Rh-Rh distance in $[Rh(CO)_2Cl]_2$ has been reported to be 3.12 Å, and the distance between the two adjacent nitrogen atoms of planar porphyrin is about 2.9 Å, it was assumed[28] that the two Rh atoms of the $[Rh(CO)_2Cl]_2$ moiety are bonded to the two adjacent nitrogen atoms of the porphyrinato core of VIII, as

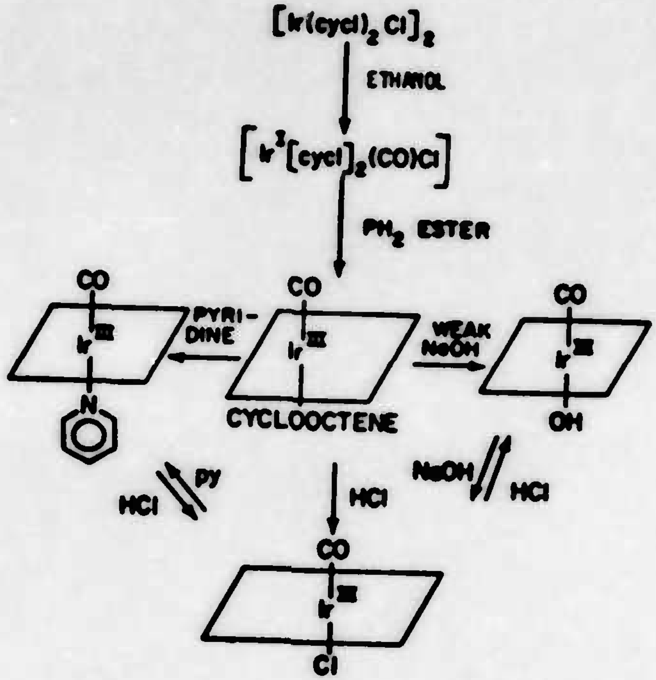


FIGURE 8

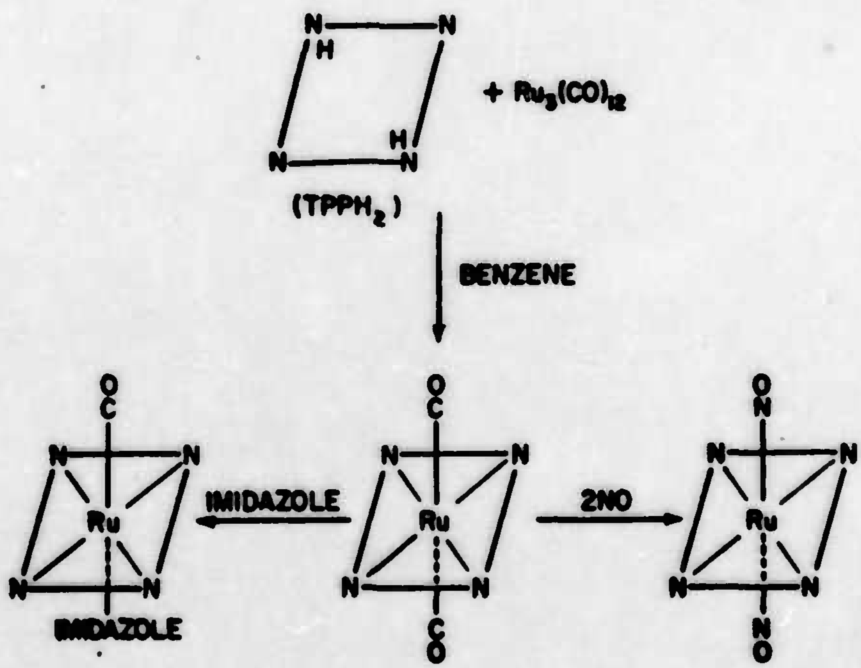
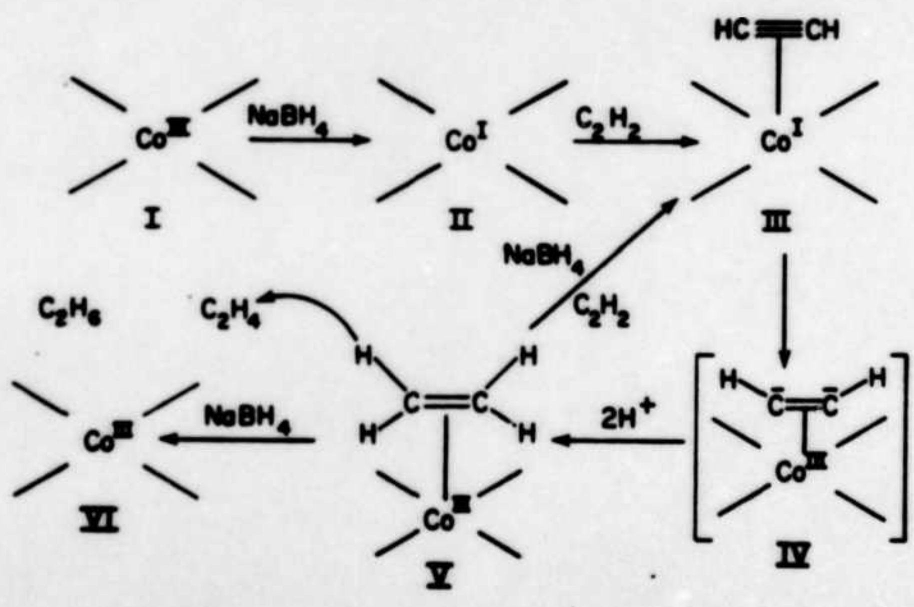


FIGURE 9

shown in Figure 9. Upon exposure to air, VII was slowly oxidized to form a rhodium(III) chloro complex of octaethylporphyrin, $Rh^{III}Cl(OEP) \cdot 2H_2O$, which can further react with alkyl lithium to give an alkyl-rhodium complex, another example of rhodium organometallo-porphyrin complex. However, VIII behaves in a different manner to give the identical alkyl-rhodium complex either by gentle heating in chloroform of chromatography on silica gell (Figure 9). This phenomenon of alkyl migration from a nitrogen atom to a metal ion is reported for the first time. The alkyl migration may proceed concertedly with oxidation of rhodium(I) to rhodium(III). The $N-CH_3$ bond fission seems to be facilitated by the aid of a low-valent rhodium ion. The reaction of (N-ethyl)octaethylporphyrin with $[Rh(CO)_2Cl]_2$ yields a rhodium(I) complex similar to VIII, which is also easily oxidized to $CH_3CH_2 \cdot Rh^{III}(OEP)$. The mechanism of metal oxidation and alkyl migration is still unknown.

Both ruthenium carbonyl, $Ru_3(CO)_{12}$, and ruthenium carbonyl halide, $[Ru(CO)_3Cl_2]_2$, react with tetraphenylporphine to give the identical product, monocarbonyl-ruthenium(II) tetra-phenyl porphine[18,21], TPPRuCO, IX. It was found that IX crystallizes with a molecule of either alcohol of water and that these weakly bound molecules are trans to the carbonyl group.[19] Recently, a single crystal x-ray diffraction analysis[18,20] confirmed this structure. Imidazole and similar organic bases complex immediately at room temperature with TPPRuCO upon mixing in benzene.[20,23] However, as expected for a low spin d^6 system, substitution reactions of the monocarbonylruthenium(II) complex take place slowly and under severe conditions to replace the carbonyl group.[24] Irradiation of degassed benzene or pyridine solutions of monocarbonyl ruthenium(II) aetioporphyrin-I pyridinate with visible of ultraviolet light leads quantitatively to a ruthenium(II) porphyrin photodimer with a metal-metal bond.[25] It is of interest that MPRuCO in benzene solution reacts smoothly with excess nitric oxide to form a dinitrosyl-ruthenium(II) meso-porphyrin complex.[17]

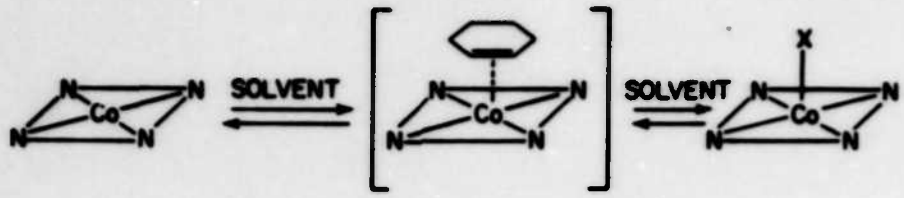
Since the successful isolation and purification of nitrogenase, the enzyme system that fixes molecular nitrogen to ammonia in living organisms, many studies have been made to find a nitrogenase model.[11,12] Fleicher and co-workers[13] created a model system consisting of the water soluble *meso*-tetra(p-sulfonatophenyl)porphinatocobalt(III), $Co^{III}TPPS$, and sodium borohydride and found it to be very effective catalyst for the reduction of the substrate of nitrogenase. For example, acetylene was reduced catalytically in this system to ethylene and ethane. A possible mechanism for this catalytic system was proposed to include cobalt-acetylene and cobalt-ethylene metalloporphyrin π-complexes as intermediates (Figure 10). For the induced oxidation of cobalt(II) mesoporphyrin IX dimethyl ester,



POSSIBLE MECHANISM FOR REDUCTION OF ACETYLENE BY A COBALT(III) PORPHYRIN SYSTEM.

FIGURE 10

Co^{II}MPIXDME by unsaturated hydroacrbons, an olefin-cobalt π-complex intermediate was proposed[14] (Figure 11). Recently, the formation of an 1:1 adduct between cobalt(II) tetra-phenylporphyrin, $Co^{II}TPP$, and carbon monoxide was reported by an esr study of a frozen



PROPOSED REACTION INTERMEDIATE FOR INDUCED OXIDATION
OF COBALT(II) PORPHYRIN BY CYCLOHEXENE

FIGURE 11

solution of toluene.[45] The paramamagtic low-spin d^7 complex of Co^{II}TPP has a single unpaired electron in the dz^2 orbital for σ bonding with carbon monoxide, which provides an opportunity for the examination by esr of σ spin delocalization to carbon monoxide. Similarly, the reversible binding of carbon monoxide to iron(II) protoporphyrin IX in piperidine was identified by its esr spectrum in frozen solution.[46]

The σ-interaction in carbon monoxide to metalloporphyrin adducts and the proposed olefin-metal π-complex intermediates for induced oxidation of Cobalt(II) porphyrin by unsaturated hydrocarbon and the catalytic reduction of acetylene in Co^{III}TPPS and $NaBH_4$ model system has brough new examples of formation of organometalloporphyrins.

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